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(54) Optical fibre manufacture

(57) The ingress of hydrogen or moisture to an optical fibre, e.g. due to pressure when the fibre is in a cable on the seabed, has a deleterious effect on the fibre's optical performance. Hence it is desirable to provide the fibres in the cable each with a hydrogen barrier. This is done by the provision of an outer layer for the fibre which includes relatively large atoms, as described of boron or an inert gas such as argon.

The methods described are:

(a) entrapping large atoms or ions, e.g. argon atoms, in the interstices of the relatively open silica crystal lattice. This method can be used in association with the application to the fibre preform of a surface layer of TiO_2/SiO_2 by a vapour phase reaction,

(b) applying a surface layer of boron carbide to the surface of the preform/fibre during the drawing,

(c) applying an outer layer of a borosilicate glass to the fibre.

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rier layer of boron carbide on the outer surface of a silica fibre preform while that preform is being drawn to produce the fibre, the boron atoms in the layer thus produced providing the hydrogen barrier.

Here also the hydrogen molecule obstructive atoms are the atoms of boron.

The first approach to the solution of the problem of hydrogen diffusion to be considered herein depends on the fact that with many glasses such as silica glass, the atomic structure is relatively open so that small atoms such as hydrogen atoms can readily pass through the material to reach the important core and optical cladding regions of the fibre. They may even, at least temporarily, take up residence in the interstices of the lattices. Such diffusion of hydrogen atoms into and through the structures, in this case of the silicon and oxygen atoms, causes the degradation of performance referred to above.

This objectionable diffusion is prevented by introducing relatively large atoms, ions or even molecules into or onto the outer region of the glass fibre. This is effected in this first approach by the creation of a gas barrier at the glass surface, i.e. the surface of the fibre preform, or of the fibre itself, either after or during drawing.

In one implementation of this approach, a preform is coated on its outer surface with a layer of a particulate, soot-like, silica by a vapour phase reaction. The soot is then consolidated to a clear glass by heating in an atmosphere which is rich in argon, which is chosen because it is an inert gas whose atoms are relatively large, but not so large as to cause stress in the surface of the glass. An example of such an atmosphere is a helium-oxygen-chlorine-argon mixture. The presence of chlorine is intended to prevent hydroxyl (-OH) formation, but is not essential provided the layer under consideration is relatively remote from the transmitting region. The other gases act in the main as carriers for the gas whose atoms are to be "stuffed" into the pores. A pressure higher than that normally used for the gaseous atmosphere at this stage of manufacture, e.g. two or three times as great, is used.

As a result of the above method, the glass forms with argon atoms entrapped in the pores of the surface glass. It will be appreciated that the time needed to complete the consolidation of the soot-like material into glass may be, and in fact usually is, lengthened due to the presence of the argon. When the outer glass layer has been thus produced, the thus-cladded preform can be drawn to fibre in the normal manner. The closer-packed atomic structure of the sintered glass retains the atoms of the inert gas both in the preform and in the fibre which results from the drawing operation.

In another version of the above method, the surface layer of the fibre is a titania/silica, TiO_2/SiO_2 layer which overlies the cladding layer of the fibre. Such a layer also tends to provide a barrier to the ingress of hydrogen and other offensive gases. The layer is applied to the outer surface of the optical fibre preform by a vapour phase reaction before the drawing of the fibre. This layer is so applied as to give the final fibre a layer of TiO_2/SiO_2 whose thickness is in the range of 5 to 20 microns. Such a layer, especially in the lower portion of its thickness range has the additional merit that it is resistant to strains due to compression. That is, it forms a compressive surface layer in the final fibre, which provides resistance to external strains. The deposition of the TiO_2/SiO_2 layer is effected with the deposition region containing the inert gas, preferably argon, under pressure, as indicated above. In this case the atoms of the inert gas enter the interstices or pores of the silica/titania structure.

As in the case in which the fibre has an outer layer of pure silica, the titania/silica layer is initially in a particulate, soot-like form and is converted to a glass by the application of heat prior to drawing. As already indicated, such a titania/silica layer provides the finished fibre with an outer layer which contributes to the hydrogen barrier action due to the fact that its atoms are large compared with the molecules of hydrogen. The layer also serves to support the "stuffed" atoms. It also provides a compressive surface coating which improves the resistance of the fibre to fatigue.

At this point it is worth referring to British Patent Specification No. 2032910B (ISEC; K.C. Kao et al 20-7). In the arrangements described therein, an optical fibre has, over its cladding, a layer of material with a lower thermal expansion coefficient than the rest of the fibre. This has been found to increase the mechanical strength of the fibre. Such an arrangement can also have a layer of higher thermal expansion material between the cladding and the just-mentioned low expansion layer. These layers can be of borosilicate with an outer silica layer or soda lime with an outer borosilicate layer.

This Patent Specification mentions that the outer layer referred to above excludes unwanted contaminants during manufacture, and among the contaminates mentioned are hydrogen and hydroxyl compounds. However, although hydrogen and hydroxyl exclusion is thus referred to, its significance in its context is in the requirement to avoid difficulties which could arise during the vapour phase reaction. What we have appreciated, which is by no means apparent from the above-mentioned Patent Specification, is that a borosilicate outer layer is also useful, if suitably applied, for use as a hydrogen barrier during the life of a cable which includes the fibre.

The borosilicate layers used in the present arrangements have relatively high boron content; thus we have appreciated that a borosilicate layer with a suitably high boron content is useful to prevent hydrogen diffusion through the glass matrix. This is because the presence of the boron atoms in a silica glass reduces the pore size for hydrogen migration, and thus provides a barrier against gas diffusion. Here also a significant point is that the boron atoms are significantly larger than hydrogen molecules.

Thus it will be seen that the borosilicate technique referred to herein, where the amount of bo-

ron present is relatively high, is in effect another aspect of the "atom stuffing" technique described above, since in both cases the hydrogen's movement is obstructed by atoms which are relatively large compared to hydrogen molecules.

We will now describe two methods of providing a borosilicate hydrogen barrier, in both of which the ratio of B_2O_3 to SiO_2 is in the range of 1 to 6 in mole per cent. The higher ratios of B_2O_3 to SiO_2 are the preferred ones.

In the first of these two methods internal vapour phase diffusion is used, a boron-oxide rich silica glass layer being deposited on the inner wall of a silica substrate tube prior to the deposition of the optical cladding and core compositions. Thus there are three stages of deposition, (i) the borosilicate layer in which the proportions of boron and silicon in the vapour are appropriate to the desired relatively high boron content of the outer layer, (ii) the cladding layer and (iii) the core layer. The latter two layers are deposited in a manner by now well established in optical fibre technology. The first layer is deposited, as indicated, using vapours with the appropriate boron percentage and with suitable carrier gases. This deposition can also to a large extent follow established technology.

After the depositions described above, the tube is collapsed to form a solid preform, which is subsequently drawn to produce the fibre. The fibre thus consists of a light-transmitting core overlayed by a lower refractive index cladding which in its turn is overlayed by the boron-oxide rich layer. The layer thus produced is a physical barrier, which is analogous to the physical barrier provided by the "stuffed" atoms of the other method described above. It is outside the region of optical field penetration in normal operating conditions, which provides a distinction between the otherwise-related borosilicate and "atom stuffing" methods.

In the method just described, a pure silica layer may, if desired, be deposited between the borosilicate glass and the deposited material of the cladding to minimise diffusion of boron into the cladding if this is considered necessary or desirable. Such a layer when used has a thickness in the range of 5 to 10 microns.

The second method of producing the borosilicate rich outer layer uses external vapour phase deposition on the surface of a preform rod. Here the borosilicate (or possibly borosilicide) glass is formed as a particulate or soot-like layer, and is subsequently fused to a solid glass layer. A surface layer of pure silica grown in a similar way, or by plasma deposition as a glass, may be applied over the barrier layer to maintain the mechanical strength and durability of the fibre.

Another approach to the use of relatively large atoms as a hydrogen barrier is to apply a layer of boron carbide to the surface of the silica fibre while drawing the fibre from the preform. It will be seen that this approach is closely related to the methods using borosilicate glass. The boron carbide depositions. The preform used is made in conventional manner, and as usual includes a doped silica core with a cladding of a lower refractive index overlaying it. This approach, like the other approaches to the provisions of a hydrogen barrier described herein, is applicable to the production of mono-mode, single mode graded index, and stepped index fibres.

The boron carbide layer, the thickness of which is in the range of 5-15 microns in the completed fibre, provides a hermetic seal against the ingress of gases including hydrogen, and also against moisture, which latter contains hydrogen. The presence of such a seal improves the fibre's reliability and prevents degradation of the fibre's optical performance in the presence of hydrogen and other gases.

It will be appreciated that the barrier layer applied to the fibre to resist the ingress of hydrogen and other unwanted gases may have dopants for other purposes, provided that they do not reduce the efficiency of the barrier as an anti-diffusant.

CLAIMS

1. A method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre, which includes the provision of a layer on or within the fibre which embodies or includes atoms or ions or molecules of relatively large size compared with the molecules of hydrogen, which relatively large atoms or ions or molecules obstruct the diffusion of hydrogen atoms into the transmitting region of the fibre, and thus act as a hydrogen barrier.

2. A method as claimed in claim 1, and in which said layer is formed by the application to the fibre or its cladding of an outer layer of a boron compound such as borosilicate having a relatively high boron content or of boron carbide having a relatively high boron content, the boron atoms being the relatively large atoms referred to in claim 1.

3. A method as claimed in claim 1 or 2, and in which the large atoms or ions are provided by introducing relatively large atoms, ions, or molecules, e.g. inert gas atoms, into the pores or interstices of the atomic lattice of the outer layer of the fibre, the atoms thus introduced forming the hydrogen barrier.

4. A method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre, which includes the introduction of atoms of relatively large size compared with the molecules of hydrogen, such as the atoms of inert gas, into the pores or interstices of part of the non-transmitting outer silica layer of the optical fibre.

5. A method as claimed in claim 4, in which the atoms to be introduced into said pores or interstices are atoms of argon, and in which said introduction is effected by the application of a gas stream under high temperature and pressure, the

drogen into a silica optical fibre, which includes applying to the preform from which the fibre is to be drawn a layer of a particulate soot by a vapour phase reaction or by a similar method, consolidating the particulate layer to a clear glass by heating under pressure in an atmosphere rich in an inert gas such as neon or argon, thus causing atoms of the inert gas to be entrapped in the pores or interstices of the glass structure of the surface glass, and thereafter drawing the preform to produce the fibre, the atoms thus entrapped forming a hydrogen barrier to substantially prevent hydrogen diffusion.

7. A method as claimed in claim 6, and in which the particulate soot is pure silica.

8. A method as claimed in claim 6, and in which the particulate soot is a titania/silica mixture.

9. A method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre, which includes producing a barrier layer of a borosilicate glass overlaying the optical cladding of the fibre, the ratio of B_2O_3 to SiO_2 in the borosilicate glass, being in the range of 1 to 6 in mole per cent, the boron atoms providing the hydrogen barrier.

10. A method as claimed in claim 9, in which internal vapour phase reaction is used to initially produce the layer of a boron-oxide rich glass layer on the inner wall of a silica substrate tube, whereafter the cladding and the core are produced, the preform made therefrom being drawn to produce the fibre.

11. A method as claimed in claim 10, and in which a layer of pure silica glass is deposited between the borosilicate layer and the cladding.

12. A method as claimed in claim 9, and in which the borosilicate layer is deposited on the outer surface of an optical fibre preform as a particulate layer and is thereafter fused to a solid glass layer, the preform thus produced being drawn to produce the fibre.

13. A method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre, which includes producing a barrier layer of a borosilicide glass overlaying the optical cladding of the fibre, the boron atoms in the borosilicide layer providing the hydrogen barrier.

14. A method as claimed in claim 13, and in which the borosilicide layer is deposited on the outer surface of an optical fibre preform as a particulate layer and is thereafter fused to a solid glass layer, the preform thus produced being drawn to produce the fibre.

15. A method as claimed in claim 9, 10, 11 or 12, and in which a surface layer of pure silica is applied over the barrier layer.

16. A method of inhibiting the diffusion of hydrogen or similar gases into a silica optical fibre, which includes producing a barrier layer of boron carbide on the outer surface of a silica fibre preform while that preform is being drawn to produce the fibre, the boron atoms of the layer thus produced providing the hydrogen barrier.

17. A method as claimed in claim 16, and in which the boron carbide is applied by a vapour phase reaction at a temperature which is relatively low compared with the temperatures used for the deposition of the cladding and core materials.

18. A method of inhibiting the diffusion of hydrogen or similar gases to a silica optical fibre, substantially as described herein.

19. A silica optical fibre to which the method of any one of claims 1 to 18 has been applied.

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SPECIFICATION

Optical fibre manufacture

This invention relates to the manufacture of optical fibre preforms and optical fibres which may be exposed to hydrogen, and to certain similar materials such as those with hydroxyl ions.

Under some circumstances hydrogen may be generated within a capable or released from the materials of the cable. The presence of this free hydrogen can have a deleterious effect on the transmission characteristics of the fibre and hence of the cable. Hydrogen can diffuse into the structure of the fibre produced by standard methods, and it has a number of effects. The major effect is to produce a vibrational absorption spectrum across a wide wavelength region. The detail of the spectrum depends inter alia on the temperature of the cable, and the partial pressure of hydrogen in the vicinity of the fibre. Limited variations in the height of the molecular hydrogen absorption peaks can arise with changes in composition but the main spectrum is unchanged. This particular mechanism is reversible.

However, other effects of hydrogen on the transmission performance are not reversible. In particular, permanent chemical changes and associated losses have been reported in fibres containing phosphorus. These changes are continuously degrading in the presence of hydrogen and increased levels of loss at peaks associated with hydroxyl ions bonded into the glass. This results, as seen by the user of such a fibre in a cable, in a considerable increase in the attenuation in the fibre.

Thus the absorption of hydrogen into the fibre, whether into its core or into its cladding, increases the attenuation which the fibre presents to the light which it is conveying. It should be noted that such hydrogen absorption by the cladding is significant in addition to absorption by the core. This is more so in the case of single mode optical fibres than for multi-mode fibres, since in the former case, as was pointed out by C.P. Sandbank, "Fiber Optic Communication: A Survey", Electrical Communications, Vol. 50, No. 1, 1975, pp 20-27, attenuation is influenced to a much greater extent by the cladding material than is the case for multi-mode transmission.

The degradation of the characteristics of the fibre due to the ingress of hydrogen is especially inconvenient when the fibres involved are in a submarine cable. In such use, it should be noted, the ingress of hydrogen and its compounds is particularly likely.

An object of the invention is to manufacture optical fibres in such ways as to provide barriers to the ingress of hydrogen gas. Thus both the spectral effects of molecular hydrogen and the permanent loss changes due to chemically induced changes related to hydrogen diffusion will be reduced to levels at which the optical performance of

method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre, which includes the provision of a layer on or within the fibre which embodies or includes atoms or ions or molecules of relatively large size compared with the molecules of hydrogen, which relatively large atoms or ions or molecules obstruct the diffusion of hydrogen atoms into the transmitting region of the fibre, and thus act as a hydrogen barrier.

In most cases the layer which includes the relatively large obstructive atoms is the outer most layer, but in some cases it may be a layer between the cladding and the light-transmissive region.

According to the invention, in a more specific form, there is provided a method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre, which includes the introduction of atoms of relatively large size compared with the molecules of hydrogen, such as the atoms of inert gas, into the pores or interstices of part of the non-transmitting outer silica layer of the optical fibre.

As will be seen from the subsequent description, the preferred gas whose atoms are to be introduced into the pores or interstices of the material is argon. This is because argon, being an inert gas, is essentially a monatomic gas, with relatively large atoms. Further it has very little chemical reactivity. The pores in the material referred to are in fact the interstices in the glass structure, in the case of silica between the silicon atoms and the oxygen atoms.

According to the invention, in another somewhat more specific form, there is also provided a method of inhibiting the diffusion of hydrogen into a silica optical fibre, which includes applying to the preform from which the fibre is to be drawn a layer of a particulate soot by a vapour phase reaction or by a similar method, consolidating the particulate layer to a clear glass by heating under pressure in an atmosphere rich in an inert gas such as neon or argon, thus causing atoms of the inert gas to be entrapped in the pores or interstices of the glass structure of the surface glass, and thereafter drawing the preform to produce the fibre, the atoms thus entrapped forming a hydrogen barrier to substantially prevent hydrogen diffusion.

According to another aspect of the invention, there is further provided a method of inhibiting the diffusion of hydrogen and similar gases into a silica optical fibre, which includes producing a barrier layer of a borosilicate glass overlaying the optical cladding of the fibre, the ratio of B_2O_3 to SiO_2 in the borosilicate glass, being in the range of 1 to 6 in mole per cent, the boron atoms providing the hydrogen barrier.

Thus in this case the relatively large atoms whose function is to obstruct the ingress of hydrogen are the boron atoms, which are large compared with the hydrogen molecules whose passage is to be obstructed.

According to yet another aspect of the invention